

A Study of the Precipitation of Gallium Hydroxide and Basic Gallium Sulfate By Means of Urea.

The Colorimetric Determination of Gallium.

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Heman Charles Fogg
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This work was undertaken at the suggestion of Professor H. H. Willard and was done under his direction in the chemistry laboratories at the University of Michigan. The Author wishes to take this opportunity to thank Dr. Willard for his many and helpful suggestions.

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The Precipitation of Basic Gallium Sulfate by Means of Urea. I. A Study of the Precipitate Produced

BY HOBART H. WILLARD AND H. C. FOGG¹

Introduction

The advantages of slow precipitation of basic salts in a homogeneous solution have been discussed by Willard and Tang.² They show that the decomposition of urea, by heating its aqueous solution, is exceedingly effective for causing a slow, uniform increase in pH and producing a dense precipitate of aluminum basic sulfate or succinate. Since the solution is homogeneous and the pH increases slowly, allowing the final value to be controlled by the duration of heating, they find it easy to obtain a much better separation of aluminum from the more basic elements than is possible using ammonium hydroxide as a precipitant.

Gallium, being closely related to aluminum chemically, would be expected to act in a somewhat similar manner when its solutions, containing ammonium chloride together with sulfate or succinate, are heated with urea.

Purification of Gallium Metal.—The metal was dissolved in hydrochloric acid and the 0.3 N acid solution saturated with hydrogen sulfide under slight pressure. The small precipitate was filtered off with the aid of paper pulp and the filtrate evaporated to small volume. This was taken up in 6 N hydrochloric acid, and extracted with cold ether previously shaken with the acid, in which gallium chloride is soluble.³ The ether was evaporated off and the remaining solution diluted with water con-

(1) Holder of the J. T. Baker Fellowship in Analytical Chemistry for the Midwestern Division during the academic year 1931-32. Present address, University of New Hampshire, Durham, N. H.

(2) H. H. Willard and N. K. Tang, *J. Am. Chem. Soc.*, **59**, 1190 (1937).

(3) E. H. Swift, *ibid.*, **46**, 2378 (1924).

taining a little hydrochloric acid and filtered. This solution was heated and treated with sufficient sodium hydroxide to redissolve the gallium hydroxide. It was then heated practically to boiling, about 1 ml. of a 1% potassium permanganate solution added, and this followed by about the same volume of alcohol.⁴ The heating was continued until the green color had disappeared and a brown precipitate of hydrated manganese dioxide had formed. Paper pulp was added and the precipitate filtered off.

The filtrate was acidified with hydrochloric acid, diluted to 1500–1800 ml., 20–25 g. of ammonium sulfate added, and the gallium precipitated by heating with urea until a pH of 4 to 5 had been reached. After filtering and washing, the precipitate was dissolved in hydrochloric acid and precipitated twice with ammonium hydroxide. The final precipitate was dissolved in perchloric acid, adding a little hydrochloric acid if the process was too slow, evaporated, and carefully heated on an air-bath to expel the excess of acid. Much care must be exercised to drive off the major part of the free acid and yet not decompose the gallium perchlorate. If the latter happens, incomplete solution will result when the salt is dissolved in water.

The gallium perchlorate was dissolved in water and electrolyzed with a current of about one ampere, using a platinum anode and a tungsten wire as a cathode. The globules of gallium which formed were allowed to fall into a small crucible placed below the electrode. Since the increase in the perchloric acid concentration during the electrolysis caused the deposition to decrease, the process was stopped after twenty-four to forty-eight hours and the liberated acid driven off as before. The gallium metal was washed with water, and the globules coalesced by adding a drop or two of hydrochloric acid. This acid was washed off with water and the latter removed by acetone.

A Study of the Dense Basic Sulfate Precipitate

It was found that when gallium solutions containing ammonium chloride, ammonium sulfate and urea were heated, the precipitate came down in a dense, granular, easily filterable form. A preliminary study of the influence of stirring and the rate of precipitation (rate of heating) on the composition of the precipitate showed that both had an appreciable effect on the ratio of gallium to sulfate. Precipitates obtained when the solutions were heated rapidly over a small flame had nearly one unit higher ratio than those formed when the precipitation was made slowly by heating in a water-bath. A precipitate formed in a solution that was gently stirred mechanically during the heating had a molar ratio of 11.18,

(4) H. N. Stokes and J. R. Cain, *ibid.*, **29**, 409 (1907).

while one from a solution which had been shaken only once or twice during the process showed a ratio of 7.43. The former precipitate, upon being rotated in contact with the original solution for twenty-four hours at room temperature, had only a slightly different ratio, *i. e.*, 11.38, while that of the latter had changed to 8.42. Stirring the solutions at greatly different rates, however, during the precipitation did not influence the composition of the precipitate to any appreciable extent. This indicates that the precipitate which settles on the bottom of the vessel does not come to equilibrium with the solution above it, and that equilibrium is reached if it is kept in suspension by even moderate stirring. The conditions, therefore, for obtaining comparable results which would most nearly represent equilibrium would be a uniform rate of heating of the solutions, accompanied by continuous stirring.

The Effect of pH on the Molar Ratio of Gallium to Sulfate.—Approximately 500 ml. of solution, 0.003 M with respect to gallium chloride, 0.02 M in ammonium sulfate and containing 4 g. of urea was placed in a wide-mouthed Erlenmeyer flask. This was heated in a boiling water-bath with constant, mechanical stirring until the desired pH had been reached, as ascertained colorimetrically with indicators on test samples withdrawn at intervals. Much attention had to be exercised in obtaining the desired pH since it might change from less than 3 to around 7 in from ten to fifteen minutes. Nor could a definite time of heating be depended upon to bring the solution to a given pH , since some solutions required fifteen to twenty minutes longer than others to reach a given value. For pH values above 7.5, the flask was closed partially by a short-stemmed funnel through which the stirrer passed to prevent the escape of too much ammonia.

When the solution had attained the desired pH , it was cooled in running water, a sample removed and the pH determined, using a glass electrode⁵ and vacuum tube potentiometer.⁶ The precipitate was filtered off, using a porcelain filtering crucible, and washed 15 times with a 1% ammonium nitrate solution, the pH of which had been adjusted to approximately that of the filtrate. It was then dried at 110 to 120°. One portion of this precipitate was ignited directly to the oxide, while another was dissolved in hydrochloric acid and the sulfate determined gravimetrically as barium sulfate. It was found that precipitation of the sulfate directly, without prior removal of the major portion of the gallium, did not introduce an error of more than a few hundredths of a milligram, even when 30 to 40 mg. of barium sulfate was precipitated.

(5) D. A. MacInnes and M. Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929); D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **52**, 29 (1930), **53**, 3315 (1931).

(6) S. E. Hill, *Science*, **73**, 529 (1931).

The concentration of the gallium in the filtrate from the basic sulfate precipitate was determined colorimetrically using quinalizarin, following the method described by Willard and Fogg.⁷

The individual results obtained are given in Table I, and the relationship between pH and the molar ratio shown graphically in Fig. 1.

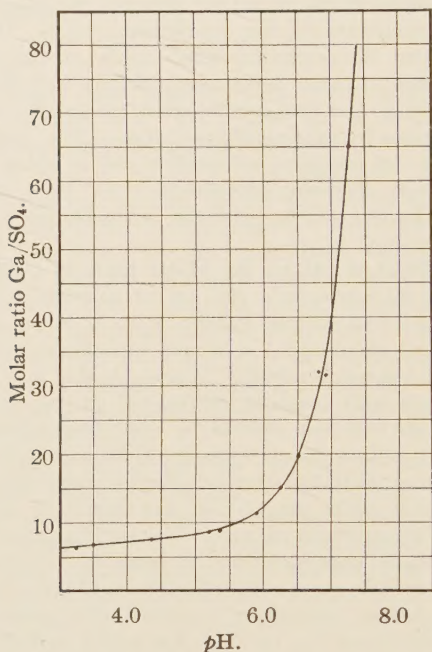


Fig. 1.—Relation between pH and ratio Ga/SO_4 .

From the table and curve it can be seen that the pH of the solution has a very decided influence upon the amount of sulfate present in the precipitate. The ratio of gallium to sulfate shows only a small increase up to a pH of about 6, but after that it increases very rapidly. The sulfate content becomes practically negligible at 7.5, while at 8.5 the precipitate is pure hydroxide. The behavior of gallium is entirely different in this respect from that of aluminum² which shows a fairly uniform increase in the ratio, with increasing pH , with no abrupt change at any point. At the higher pH values the aluminum precipitate contains decidedly more sulfate.

(7) H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

Although the amount of gallium left in the filtrate shows many irregularities, there is no doubt about its being a minimum between the pH values of 4 and 5.5. This has been amply confirmed by many determinations of gallium in filtrates from actual quantitative precipitations made by urea.

Approaching the Equilibrium from Each Direction. The Replacement of Sulfate by Hydroxyl.—Since the sulfate content of a precipitate, removed from a solution of pH 7.5, or above, is so low, it would seem as if that which is present in a precipitate obtained at a low pH would be removed easily by digesting in a solution of higher pH . Accordingly, some precipitates were formed

TABLE I
RELATION BETWEEN pH , THE MOLAR RATIO Ga/SO_4 , AND
THE SOLUBILITY OF THE BASIC SULFATE
Concentration of Ga , 0.003 M ; of $(NH_4)_2SO_4$, 0.02 M

No.	pH	Atoms of Ga / moles of SO_4	Ga in filtrate, mg./liter
1	3.26	6.35	4.0
2	3.53	6.81	2.0
3	4.35	7.46	0.2
4	5.19	8.41	.06
5	5.36	8.33	.2
6	5.91	11.28	.8
7	6.24	14.90	2.0
8	6.53	19.51	2.7
9	6.80	32.10	3.3
10	6.91	31.58	1.0
11	7.28	64.93	7.0
12	7.36	1075	7.0
13	7.46	1628	
14	8.48	α	

in the usual manner, the digestion being stopped when the pH was 5 or 6. After cooling and settling, the solution was decanted and replaced by a 0.02 M ammonium sulfate solution, the pH of which had been brought previously to about 7 by heating with 4 g. of urea. The mixture was heated and stirred as before for six and one-half hours. The precipitate was filtered off, the pH of the filtrate, and the molar ratio in the precipitate determined as before. With sample No. 3 the procedure was the same except that the mixture was placed in a bottle and rotated at room

temperature for ninety-two hours, instead of being heated. The results are collected in Table II.

TABLE II
THE REPLACEMENT OF SULFATE BY HYDROXYL

Number	1	2	3
Original pH	5.89	4.80	5.89
Ratio Ga/SO ₄ at orig. pH ^a	10.5	7.9	10.5
Final pH	7.61	7.68	7.34
Ratio Ga/SO ₄ at final pH	1009	1219	399

^a Values taken from Fig. 1.

These results show that sulfate in a basic gallium sulfate precipitate is so easily removed that agitation, even at room temperature, with a solution of higher pH will serve to take out a large proportion.

The Replacement of Hydroxyl by Sulfate.—A precipitate obtained from a solution of pH 8.68 was rotated in a bottle at room temperature for one hundred and eighty-six hours, in contact with 0.02 *M* ammonium sulfate solution which had a pH of approximately 3. At the end of this time the precipitate was filtered off and the ratio of gallium to sulfate in the precipitate, as well as the pH of the filtrate, determined.

SUMMARY OF DATA

Original pH	8.68
Ratio Ga/SO ₄ at original pH	∞
Final pH	3.26
Ratio Ga/SO ₄ at final pH	2997

This shows that the replacement of hydroxyl by sulfate in a precipitate of gallium hydroxide takes place very slowly.

The Effect of a Higher Concentration of Ammonium Sulfate on the Molar Ratio.—This effect was ascertained by the procedure described under the determination of the molar ratio, except that the solution was 0.2 *M* in ammonium sulfate. The data obtained are given in Table III.

The results show that increasing the concentration of sulfate ion present in the solution has only a slight influence in increasing the proportion of that radical to be found in the precipitate.

TABLE III
THE EFFECT ON THE MOLAR RATIO OF VARYING THE
CONCENTRATION OF AMMONIUM SULFATE

Number	1	2	3	4
pH	3.7	4.11	5.3	5.35
Ratio Ga/SO ₄ with 0.02 <i>M</i> (NH ₄) ₂ SO ₄ ^a	7.0	7.4	8.1	8.2
Ratio Ga/SO ₄ with 0.2 <i>M</i> (NH ₄) ₂ SO ₄	7.49	7.93	9.09	8.94
Difference in ratio	+0.5	+0.5	+1.0	+0.7

^a Values taken from Fig. 1.

Summary

1. The composition of the dense gallium basic sulfate precipitated by urea from a solution containing sulfate varied from pure hydroxide at a pH of 8.5 to one containing a considerable portion of sulfate at a pH of 3.3.

2. Digestion in a solution of higher pH removed sulfate readily; the reverse process was extremely slow.

3. Precipitation of gallium with urea in 0.02 *M* ammonium sulfate solution is most complete at a final pH between 4 and 5.5; under these conditions about 0.2 mg. of gallium per liter remains in solution.

The Precipitation of Basic Gallium Sulfate by Means of Urea. II. The Separation and Determination of Gallium

BY HOBART H. WILLARD AND H. C. FOGG¹

Introduction.—It has been shown by Willard and Tang² that aluminum can be precipitated quantitatively by heating its solution with urea in the presence of ammonium chloride and ammonium sulfate or succinate. This method gives a much better separation of this element from the more basic elements such as zinc, nickel, cobalt, manganese, etc., than does an ammonium hydroxide precipitation. Willard and Fogg³ found that a similar dense precipitate of basic sulfate was formed when gallium solutions were heated with urea, ammonium chloride and ammonium sulfate. In this latter instance, it was found that only about 0.2 mg. of gallium per liter remained dissolved if the final pH of the solution was 4 to 5.5, which is considerably less than the amount which remains when gallium is precipitated with ammonium hydroxide in the presence of ammonium salts.⁴

The common method of precipitating gallium hydroxide with ammonium hydroxide, followed by ignition to the oxide, has been investigated and discussed by Fricke and Meyring.⁵ During careless ignition, the oxide may be reduced to the volatile metal by hot carbon, and such reduction always occurs if in contact with platinum.^{4,5} Every trace of chloride must be washed out of the

(1) Holder of the J. T. Baker Fellowship in Analytical Chemistry for the Mid-western Division during the academic year, 1931-1932. Present address: University of New Hampshire, Durham, N. H.

(2) H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1937).

(3) H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 1197 (1937).

(4) L. Moser and A. Brukl, *Monatsh.*, **50**, 181-192 (1928).

(5) R. Fricke and K. Meyring, *Z. anorg. allgem. Chem.*, **176**, 325-348 (1928).

precipitate since ammonium chloride reacts with gallium oxide, even at 250° , to form volatile gallium trichloride.

The Quantitative Precipitation of Gallium by Urea

Preliminary Work.—Preliminary work on the quantitative precipitation gave considerable information regarding some of the errors which would affect the accuracy of the results.

(a) It was found necessary to heat the gallium oxide to 1200° for one hour to obtain constant weight. No loss in weight resulted from this treatment. It was also found that great care must be used to avoid loss when the precipitate was ignited in the presence of paper.

(b) The presence of chloride in the solution from which the precipitation was made, always caused low results. This is doubtless due to some of the gallium precipitating as basic chloride, and volatilizing as the chloride, during ignition. When the metal was dissolved in hydrochloric acid, evaporated to *incipient* fuming with sulfuric acid, and the determination completed as described later, losses of 3 to 7 mg. occurred.

(c) Cold water was best for washing the precipitate of basic gallium sulfate, since it was more soluble in wash solutions containing ammonium salts.

(d) The amount of gallium remaining in solution after precipitation was much less if the cover glass was raised on hooks during the heating of the solution, so as to allow the escape of carbon dioxide. The weight of gallium, calculated as oxide, left in the filtrates after precipitation was found to be: with cover glass on beaker in usual manner, 0.70 mg./l. (average of 7); with cover glass raised on hooks, 0.33 mg./l. (average of 32).

(e) The most favorable pH for quantitative precipitation was found to be between 4 and 5.5.

(f) The precipitate was somewhat flocculent, but not at all gelatinous, and had an appreciable tendency to adhere to the beaker, regardless of whether the latter was of glass or of silica.

Precipitation of Gallium from a Sulfate Solution

Procedure.—The sample of gallium metal purified as described by Willard and Fogg³ was transferred to a 600-ml. beaker and dissolved by warming with 3 ml. of concentrated sulfuric acid on a hot-plate. After about twelve hours a little water was added, the solution evaporated and heated again, to make certain that all of the metal had been attacked; 150 to 200 ml. of water and 3 g. of urea, as a filtered solution, were added. After diluting to nearly 500 ml., redistilled ammonium hydroxide was added dropwise until the solution was almost permanently

turbid. It was then heated to incipient boiling and kept at that temperature until a sample of the solution showed that the pH was between 4 and 5.5 (barely alkaline to methyl orange). When the desired pH had been reached the solution was filtered through a weighed porcelain filtering crucible, the precipitate washed with cold water and ignited at 850°. After weighing, most of the oxide was transferred to an unglazed porcelain crucible, ignited for one hour at 1200° and again weighed. From the loss in weight the corrected weight of the entire precipitate was calculated. This method was adopted because the filtering crucible could not be heated to this temperature, and it was desired to avoid any possibility of reduction by carbon.

The pH of the filtrate was determined by means of a set of approximately isohydric indicators.⁶ The gallium which remained in the filtrate and wash water, and which adhered to the beaker after as thorough removal as possible with a policeman, was determined colorimetrically by the method described by Willard and Fogg.⁷ Table I shows the results obtained following the above procedure.

TABLE I
THE DETERMINATION OF GALLIUM BY PRECIPITATION AS
BASIC SULFATE

Weight of gallium oxide taken, approximately 0.13 g.

pH	Wt. Ga ₂ O ₃ from filtrate and beaker, g.	Error Ga ₂ O ₃ , mg.
6.1	0.00073	-0.25
5.6	.00088	- .23
5.3	.00078	+ .15
5.8	.00096	± .00
6.1	.00070	- .25
5.0	.00059	- .21
4.3	.00072	- .18
4.4	.00046	- .21

Discussion of Results.—It can be seen that gallium can be determined quantitatively by precipitation from a sulfate solution by heating with urea. Although the precipitate is not quite as insoluble as could be desired, it is nevertheless much less soluble than the hydroxide. As a rule from 0.1 to 0.2 mg., calculated as oxide, remained in the 500 ml. of filtrate, and approximately 0.01 mg. was dissolved by 150 to 200 ml. of wash water. The most troublesome feature was the

(6) S. F. Acree and E. H. Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

(7) H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

tendency of the precipitate to adhere to the beaker. From 0.1 to 0.6 mg. of oxide would remain even after a most thorough cleaning with a policeman.

The Precipitation of Gallium from a Buffered Solution.—Since so much difficulty was encountered in controlling the pH with no buffer in the solution, a number of determinations were made with varying amounts of succinate or acetate present. The above procedure was followed

TABLE II

THE DETERMINATION OF GALLIUM BY PRECIPITATION FROM A SOLUTION BUFFERED WITH ACETATE OR SUCCINATE

Weight of gallium taken, approximately 0.13 g.				
Ammonium acetate added, g.	Time of heating, hrs.	pH	Wt. Ga_2O_3 from filtrate and beaker, g.	Error Ga_2O_3 mg.
3	3.5	4.7	0.00069	-0.23
3	3.5	4.6	.00078	- .03
2	2.5	4.6	.00088	+ .15
2	2.5	4.5	.00081	- .14
Succinic acid added				
5	2	4.0	.00177	- .08
2	2.5	4.1	.00140	- .06
1	2.5	5.5	.00093	- .32

except that varying amounts of succinic acid or ammonium acetate, and 4 g. of urea, instead of 3, were added and the solutions heated for the time given. The results are shown in Table II.

Discussion of Results.—The amount of gallium recovered, using the two buffers, was in as good agreement with the quantity taken as when only sulfate was present. However, the concentration of gallium left in the filtrate was much greater than with sulfate, varying from 0.6 mg. to as much as 3.0 mg. per liter. This is not entirely obvious from the data listed, since in some instances the precipitation was made from a smaller volume.

The Separation of Gallium from Other Elements by Precipitation from Sulfate Solution

Separation from Calcium.—The determination of gallium in gallium-calcium mixtures was made following the procedure first described. The cal-

cium in the ignited oxide was determined by dissolving in hydrochloric acid and precipitating as oxalate in the usual manner. The results in Table III show that gallium can be separated from calcium by this method if there is not enough of the latter element present to exceed the solubility of calcium sulfate at the final pH. With approximately 500 ml. of solution, and 0.2 g. of calcium, less than 0.1 mg. was carried down, but if 0.3 g. is present, a considerable quantity accompanies the gallium.

TABLE III
THE DETERMINATION OF GALLIUM IN THE PRESENCE OF
CALCIUM

Weight of gallium, approximately 0.13 g.

pH	Ca taken, g.	Ga ₂ O ₃ from filtrate and beaker, g.	Error Ga ₂ O ₃ , mg.
3.9	0.05	0.00083	-0.10
4.1	.075	.00066	+ .16
4.4	.075	.00035	- .04
5.4	.10	.00037	+ .07
4.0	.10	.00039	+ .26
4.3	.20	.00072	+ .05
5.8	.20	.00037	- .20

Separation of Zinc.—According to Britton⁸ zinc begins to precipitate at a pH of 5.2. Even though this is not much higher than that required for the precipitation of basic gallium sulfate, a good separation is effected.

The results shown in Table IV were obtained by the method previously given. To determine the zinc which accompanied the gallium, the final ignited oxide was dissolved by warming with concentrated hydrochloric acid and the zinc precipitated as sulfide from citric acid solution, using calcium citrate as a collector, as recommended by Bodansky.⁹ It was then determined turbidimetrically with potassium ferrocyanide according to the method of Breyer.¹⁰

Separation from Manganese.—Since this ele-

(8) H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1932, p. 325; *J. Chem. Soc.*, **127**, [2] 2110-2159 (1925).

(9) M. Bodansky, *Ind. Eng. Chem.*, **13**, 696 (1921).

(10) F. G. Breyer, in Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., New York, 1925, p. 607.

ment begins to precipitate at a pH of 8.5, it is readily separated from gallium by heating with urea. Table IV shows the results obtained, following the procedure already given. The manganese carried down by the gallium was determined colorimetrically.

TABLE IV
THE DETERMINATION OF GALLIUM IN THE PRESENCE OF
ZINC AND MANGANESE

pH	Zn taken, g.	In ppt., mg., ZnO	Ga ₂ O ₃ from filtrate and beaker, g.	Ga ₂ O ₃ taken, g.	Error Ga ₂ O ₃ mg.
4.5	0.01	0.05	0.00026	0.13496	-0.20
4.5	.015	None	.00057	.13268	- .06
4.4	.015	0.05	.00022	.13207	- .15
4.2	.025	.15	.00054	.12750	- .21
4.4	.025	.07	.00025	.13247	+ .01
4.5	.05	.60	.00093	.13832	- .14
5.6	.10	1.00	.00055	.13127	- .07
4.4	.25	0.63	.00036	.12703	+ .25
4.1	.50	0.90	.00075	.13752	- .02
4.7	1.00	2.00	.00027	.13214	- .02
4.3	0.5	0.05	.00033	.03784	+ .14
4.6	0.5	.07	.00016	.03475	+ .09
5.9	1.0	.07	.00090	.01371	- .43
5.7	1.0	.25	.00032	.02178	- .36
4.7	1.0	.05	.00022	.01425	+ .12
5.9					
4.0	1.0	None ^a	.00182	.13765	+ .07
4.6					
5.6	1.0	0.05 ^a	.00071	.13711	$\pm$.00
5.1					
4.2	1.0	None ^a	.00127	.13664	- .17
5.6					
4.7	1.0	None ^a	.00123	.13490	- .27
	Mn	Mn ₂ O ₄			
4.8	0.5	0.05	0.00026	0.12307	-0.01
4.2	.5	.07	.00021	.13416	- .12
4.8	.5	.12	.00021	.13116	+ .08
4.7	.5	.11	.00021	.13419	+ .19
4.4	1.0	.23	.00095	.13496	- .11
5.2	1.0	.32	.00025	.13429	+ .08
4.2	1.0	.20	.00024	.13342	- .13
4.4					
4.3	1.25	.01 ^a	.00053	.13220	+ .18
4.5					
5.3	1.25	.01 ^a	.00044	.13684	- .15

^a Two precipitations.

Discussion of Results.—Using a volume of about 500 ml., one precipitation will satisfactorily

separate 0.1 g. of gallium from 0.02 g. of zinc or a few milligrams of gallium from 1 g. of the latter. If as much as 1 g. of zinc is present with the larger amount of gallium, a reprecipitation will remove all of it. Using 500 ml. of solution, 0.1 g. of gallium can be separated from as much as 0.5 g. of manganese by a single precipitation, with only 0.1 mg. of manganese oxide accompanying the precipitate. If 1.0 g. of manganese is present, somewhat more will be found with the gallium. A double precipitation gives complete separation, even when 1.25 g. is present. Undoubtedly an equally good separation would be obtained from magnesium, although this was not studied.

Summary

Gallium can be precipitated quantitatively as basic sulfate by heating its sulfate solution, containing 3 g. of urea, until a pH of 4 to 5.5, or possibly 6, has been reached. If the solution contains acetate or succinate, more gallium remains in solution. Employing the procedure developed, it was found possible to separate gallium from 1 g. of zinc and manganese and 0.2 g. of calcium. Obviously weaker bases than these such as aluminum, chromium and iron will interfere. Magnesium should not interfere.

The Separation of Gallium and its Colorimetric Determination by Means of Quinalizarin¹

BY H. H. WILLARD AND H. C. FOGG²

Practically the only method available for the detection and estimation of small amounts of gallium is by means of the spectroscope. This furnishes a specific and sensitive method for detection, and one which in the hands of experienced manipulators is quite accurate for its determination. However, it has the disadvantages of requiring an apparatus which not all laboratories possess, and a technique which everyone has not had an opportunity to develop.

Dennis and Bridgman³ using a spark were able to detect, by means of a direct vision spectroscope, the gallium line, 4172, in a concentration of 3 mg. of gallium per 100 ml. when 0.15 ml. of the solution, corresponding to 0.0046 mg. of gallium, was placed in the small cup used to hold the solution. Approximately five times this amount of gallium was required for the line 4033 to be visible. The spectrograph has also been employed by Papish and Holt⁴ for the direct detection and semi-quantitative estimation of gallium in certain minerals. Kimura, Nakamura and Kusibe⁵ combined chemical concentration with the spectrographic method for the qualitative examination of a large number of Japanese minerals for gallium.

A colorimetric method, even if not as specific,

(1) This manuscript was originally received on August 14, 1933, but was withdrawn and resubmitted after additional experimental work had been done.—EDITOR.

(2) Holder of the J. T. Baker Chemical Company Fellowship in Analytical Chemistry for the Mid-Western Division for the academic year, 1931-1932.

(3) Dennis and Bridgman, *J. Am. Chem. Soc.*, **40**, 1531 (1918).

(4) Papish and Holt, *J. Phys. Chem.*, **32**, 142 (1928).

(5) Kimura, Nakamura and Kusibe, *J. Chem. Soc. Japan*, **52**, 55-62 (1931).

is desirable and an investigation was, therefore, made to find a dye which would form with gallium, a suitable lake.

Experimental

Aurin tricarboxylic acid, alizarin red-S, titan yellow and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) were tried. Although the first dye gave a color with small amounts of gallium, as stated by Corey and Rogers,⁶ no suitable experimental conditions could be established which would allow an accurate colorimetric determination.

Alizarin red-S gave a pink to salmon color in buffered solutions. However, the limits of pH range, from 4.0 to 4.5, were so narrow and the effect of varying concentrations of buffer salts so great that it was practically valueless as a reagent. Titan yellow gave no color with gallium. Quinalizarin gave a pink to amethyst color, depending upon the concentration of gallium and the pH of the solution. Kolthoff⁷ has suggested this last reagent as a sensitive test for aluminum.

Preliminary Investigation of Quinalizarin.—This preliminary work showed that: (a) gallium produced a distinct color in the pH range of 4.5 to 6.0, and that the most favorable condition, considering the effect of aluminum, etc., was a pH of 5.0; (b) the addition of ammonium acetate or ammonium succinate increased the intensity of color of the dye alone and also of solutions containing gallium to about the same extent; (c) the presence of ammonium chloride made the difference in color between the blank and gallium solutions somewhat more pronounced; (d) in general the most uniform results could be obtained if the solutions had a pH of 5 and were normal in ammonium acetate and half normal in ammonium chloride.

Action of Quinalizarin with Other Ions.—Qualitative tests in a solution of pH 5.0, normal in ammonium acetate and half normal in ammonium chloride showed that: iron (Fe^{+++}), tin (Sn^{++}), antimony (Sb^{+++}), copper (Cu^{++}), lead (Pb^{++}), indium (In^{+++}), germanium (Ge^{++++}), vanadyl (VO^{++}), vanadate (VO_3^-) and molybdate (MoO_4^{--}) give colors which are not completely inhibited by fluoride. Iron (Fe^{+++}) and lead (Pb^{++}) cause a blue color while the others are pink. All are very sensitive. Zirconium (Zr^{++++}), thorium (Th^{++++}) and the rare earths give a blue, while tin (Sn^{++++}), beryllium (Be^{++}), aluminum (Al^{+++}), thallium (Tl^{+++}), titanium (Ti^{++++}), arsenite (AsO_3^{--}) and antimonate (SbO_4^{--}) cause a pink color which can be prevented by the addition of fluoride. The alkalis, alkaline earths, magnesium (Mg^{++}), manganese (Mn^{++}), iron (Fe^{++}), mercury (Hg^{++}), thal-

(6) Corey and Rogers, *J. Am. Chem. Soc.*, **49**, 216 (1927).

(7) Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 360 (1928).

lithium (Li^+), cadmium (Cd^{++}), uranyl (UO_2^{++}), tungstate (WO_4^{--}) and arsenate (AsO_4^{--}) give rise to no color. Silver (Ag^+), mercury (Hg^+), bismuth (Bi^{+++}), tantalum (Ta^{++++}) and columbium (Cb^{++++}), either precipitate as chlorides or hydrolyze out, thus causing no interference after removal by filtration. Cobalt (Co^{++}), nickel (Ni^{++}) and chromium (Cr^{+++}) do not interfere except for their own color. Zinc (Zn^{++}) can be present to the extent of 0.5 g. per liter before any color can be seen. More than that gives an amethyst to blue color.

Influence of Various Acid Radicals on the Color Produced by Gallium (Ga^{+++}), Iron (Fe^{+++}) and Aluminum (Al^{+++}).—Citrate, oxalate and tartrate effectively prevented the formation of color in all cases.

Phosphate had no effect on the color produced by aluminum but prevented the color due to ferric iron if added in sufficient concentration. However, it caused a very appreciable decrease in the color given by gallium.

Fluoride effectively prevented the color given by aluminum, while exerting only a relatively small influence in the case of iron and gallium. The only effect with gallium was a slight decrease in the intensity of color in all solutions, including the blank (see Table I). Experiments showed that 0.5 g. of sodium fluoride per liter, in excess of that required to form Na_3AlF_6 , was necessary for the complete prevention of lake formation by aluminum. This was also about the maximum concentration of sodium fluoride permissible without seriously decreasing the color caused by gallium.

The Limit of Sensitivity for Gallium, Ferric Iron, Aluminum, Zinc and Indium.—This was determined by comparison of 50 ml. of solution in 50-ml. Nessler tubes, 125 mm. to the mark, the source of light being G. E. daylight bulbs, diffused by a ground glass plate. All solutions were *N* in ammonium acetate, 0.5 *N* in ammonium chloride and had a *pH* of 5.0 ± 0.1 determined with a quinhydrone electrode. One series contained no sodium fluoride while the other contained 0.5 g. per liter. One ml. of a 0.01% alcoholic solution of quinalizarin was added. The figures given below represent the concentrations of the ions which gave sufficient color to be distinguished with certainty from the blank upon repeated determinations.

TABLE I
LIMIT OF DETECTION OF Ga, Al, Fe^{+++} , Zn AND In WITH
QUINALIZARIN

Metal	NaF, 0.5 g./l. metal mg./l.	No NaF, metal mg./l.
Ga	0.02	0.02
Al	20.00	.12
Fe (ic)	0.05	.02
Zn	800.00	400.00
In	10.00	2.00

Since it is obvious that a satisfactory colorimetric determination of gallium is possible only after a separation from many other metals, a study of such separations is described in the following pages. The most difficult and important separations, such as those from aluminum, iron and indium, are so different that they must be treated separately. The usefulness of the method is considerably reduced by the difficulty in removing iron, but many cases are encountered in which only very small amounts of iron are present.

The Determination of Gallium in the Presence of Aluminum

The Influence of Various Salts and pH on the Separation of Aluminum from Gallium by Means of Sodium Fluoride.

—Qualitative and semi-quantitative tests showed that the presence of ammonium chloride, ammonium acetate, the pH of the solution at the time of addition of sodium fluoride, the excess of sodium fluoride and the presence of much sodium or potassium salt influenced the separation of aluminum and the recovery of gallium. Extensive experiments showed that the best separation of aluminum, by precipitation as Na_3AlF_6 , was obtained when sodium fluoride was added as a saturated solution to the solution containing aluminum and gallium which was about half normal in ammonium chloride and buffered with ammonium acetate to a pH of around 5. The presence of more than a few milligrams of potassium or 100 mg. of sodium ion was detrimental to the above separation, although neither potassium nor sodium interfered with the colorimetric part of the determination.

Procedure.—The solution containing gallium and aluminum is neutralized to turbidity with ammonium hydroxide, cleared with 6 N hydrochloric acid, and 4 ml. in excess added. This is followed by 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride. (This will make the solution N in ammonium acetate, 0.5 N in ammonium chloride, and give a pH of nearly 5.0 when finally diluted to 100 ml.) After diluting to 70–80 ml. and heating to 70–80°, enough saturated sodium fluoride solution is added, while stirring, to form Na_3AlF_6 and leave 0.5 g. per liter in excess. The resulting precipitate should be of a fine, crystalline nature. If it is of the opalescent, almost invisible type, some of the gallium is practically certain to be retained or else the aluminum may not be removed entirely. When it has stood for one to one and a half hours, with occasional stirring, paper pulp is added, the precipitate filtered off, the filtrate diluted to 100 ml. and adjusted to a pH of 5.0 using a quinhydrone electrode. Aliquot portions of such volume as to contain from 0.001 to 0.01 mg. of gallium are placed in 50-ml. Nessler tubes and filled to the mark with the stock solution from which the standards are made. A series of standards is prepared by adding to 50-ml. portions of this solution in Nessler tubes,

definite volumes of a standard gallium chloride solution containing 0.01 mg. of gallium per ml. One ml. of a 0.01% alcoholic solution of quinalizarin is added to each tube, the contents stirred and the colors compared after one or two minutes.

Using 50-ml. Nessler tubes, the best concentration for comparison lies between 0.02 and 0.2 mg. of gallium per liter. Between 0.02 and 0.08 mg. per liter, a difference of 0.01 mg. per liter can be detected easily. Above that, it requires a difference of 0.02 mg. per liter.

The quinalizarin solution is not very stable and becomes practically useless after it has been prepared a week. Neither is it much good directly after preparation. It gives the best results from one to four days after preparation.

It is not necessary that the solutions have a pH of exactly 5.0, but it is necessary that both standards and unknown have the same pH. A very great deviation from 5 is not recommended, however, since at 4.5 the sensitivity of the gallium is much less, while at a higher pH the sensitivity of aluminum is greater.

The presence of 0.5 g. of sodium fluoride per liter is to be recommended in all cases, even if a separation of aluminum has not been made, since it will prevent any color due to traces of that element which are almost certain to be present.

The results shown in Table II, numbers 1 to 10, were obtained by the above method, while numbers 11 to 15 were obtained without preliminary separation of aluminum.

From this it is seen that gallium can be separated accurately from aluminum if not more than 10 mg. of the latter is present. If the concentration of aluminum is not greater than 15 mg. per liter, the gallium can be determined directly without a preliminary precipitation of aluminum as Na_3AlF_6 .

The Determination of Gallium in the Presence of Iron and Indium

Since quinalizarin gives a very sensitive color reaction with ferric iron, it is essential that every trace of this ion be removed before proceeding with the colorimetric determination of gallium. Experiments showed that it was not possible to convert the iron into ferrocyanide and determine the gallium directly, nor to collect quantitatively the latter from a solution by precipitating it along with cadmium sulfide. When the iron was reduced before adding quinalizarin, it was found that the reducing agents such as bisulfite, hydrazine sulfate and hydroxylamine hydrochloride failed to cause complete reduction. Others, like sodium hydrosulfite and phenylhydrazine hydrochloride, destroyed the dye.

TABLE II
DETERMINATION OF GALLIUM IN THE PRESENCE OF ALU-
MINUM

No.	Al, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10	0.000	0.000	±0.000
2	10	.005	.0047	— .0003
3	10	.010	.011	+ .001
4	10	.010	.012	+ .002
5	10	.010	.010	± .000
6	10	.020	.021	+ .001
7	10	.050	.047	— .003
8	20	.000	.000	± .000
9	20	.010	.0075	— .0025
10	20	.010	.006	— .004
	Al, mg./50 ml.	Ga taken, mg./50 ml.		
11	0.75	0.000	0.000	±0.000
12	.75	.0005 ^a	.000	— .0005
13	.75	.001	.0011	+ .0001
14	.75	.0025	.0028	+ .0003
15	.75	.005	.005	± .000

^a 0.0005 mg. of gallium in 50 ml. of solution is beyond the limit of sensitivity of the test.

The Separation of Iron and Indium from Gallium by Means of an Excess of Sodium Hydroxide.—Although this is a standard method of separation in ordinary analytical work, two serious difficulties were encountered in this instance. First, the adsorptive properties of ferric hydroxide proved to be so great that more than 1 mg. of iron prevented complete recovery of the gallium. Second, sufficient ferric hydroxide to give a color with the dye remained in the colloidal state and passed through the filter, even though the precipitate was settled by centrifuging, and removed by the method recommended by Cox, Schwartz, Hahn, Unangst and Neal,⁸ for the separation of iron and aluminum. However, the use of hydrated manganese dioxide as a collector according to the method of Stokes and Cain⁹ was found to give entirely satisfactory results for both iron and indium.

Procedure.—The solution containing the iron and gallium in 25 ml. or less, was heated nearly to boiling and enough approximately 3 *N* sodium hydroxide added to make the final concentration between half normal and normal. The heating was continued until the ferric hydroxide had coagulated. Paper pulp was added, the precipitate filtered off and washed with a hot 1% sodium chloride solution made alkaline with sodium hydroxide. The paper pulp and filter paper used in this, and the next,

(8) Cox, Schwartz, Hahn, Unangst and Neal, *Ind. Eng. Chem.*, **24**, 403 (1932).

(9) Stokes and Cain, *J. Am. Chem. Soc.*, **29**, 409 (1907).

filtration had been treated with hot 1.5 *N* sodium hydroxide solution and then washed with water. The filtrate was heated nearly to boiling, eight to ten drops of a 1% potassium permanganate solution added, and this followed in a minute or two by enough alcohol (5 to 10 drops) to cause reduction. The heating was continued until all green color had disappeared, and the brown precipitate of hydrated manganese dioxide had formed. This was filtered off and washed as before. The filtrate was neutralized to litmus with hydrochloric acid and enough ammonium chloride, ammonium acetate and sodium fluoride introduced so that the *pH* of the solution and the salt concentration would have the values previously recommended, when the whole was diluted to the desired volume (100 or 250 ml.). This was most conveniently done by adding the sodium fluoride as a saturated solution, and the other two salts as a stock solution with a *pH* of 5, which was 1.5 *N* in the former and 3 *N* in the latter.

In the case of indium the precipitate need not be filtered off before adding the permanganate.

The gallium was then determined as described under "The Determination of Gallium in the Presence of Aluminum." Table III shows the results obtained using the above procedure.

TABLE III
THE SEPARATION OF GALLIUM FROM IRON AND INDIUM

No.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	0.5	0.010	0.009	-0.001
2	.5	.020	.018	- .002
3	1.0	.000	.000	± .000
4	1.0	.005	.006	+ .001
5	1.0	.020	.020	± .000
6	1.0	.060	.058	- .002
7	2.0	.010	.005	- .005
8	2.5	.010	.008	- .002
9	20.0	.010	.003	- .007
10	0.0	.010	.009	- .001
11	.1	.010	.010	± .000
12	.2	.000	.000	± .000
13	.2	.005	.0055	+ .0005
14	.2	.010	.012	+ .002
15	.2	.050	.048	- .002
In, mg.				
16	100	.000	.000	± .000
17	100	.010	.011	+ .001
18	100	.025	.028	+ .003
19	100	.050	.052	+ .002
20	100	.060	.058	- .002

In numbers 10 to 20 the precipitate of ferric hydroxide, or indium hydroxide, was not filtered off before adding the potassium permanganate and reducing.

From this it can be seen that gallium can be determined accurately in the presence of iron, using the method given, only when not more than 1 mg. of the latter is present; otherwise a very appreciable amount of the gallium will be lost. Determinations 10 to 15 show that if not more than 0.2 mg. of iron is present, it is unnecessary to filter off the ferric hydroxide before adding the permanganate. With larger amounts of iron, it was found that it was removed incompletely unless filtered off as recommended in the procedure. Indium gives no difficulty even when 100 mg. is present.

Data obtained, but not included in the table, showed that if the concentration of indium did not exceed 8 mg. per liter, accurate determinations of gallium could be made without a preliminary separation.

The Determination of Gallium in the Presence of Zinc and Aluminum or Iron

Since preliminary determinations, Table I, showed that nearly 600 mg. of zinc per liter gave no color with quinalizarin if 0.5 g. of sodium fluoride was present, no special procedure was necessary for determining gallium in the presence of this element.

TABLE IV
THE DETERMINATION OF GALLIUM IN THE PRESENCE OF
ZINC AND IRON OR ALUMINUM

No.	Al, mg.	Zn, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1		25.0	0.000	0.000	± 0.000
2		25.0	.001	.0012	+ .0002
3		25.0	.005	.006	+ .001
4		50.0	.010	.010	$\pm .000$
5		50.0	.020	.020	$\pm .000$
6	10.0	20.0	.000	.000	$\pm .000$
7	10.0	10.0	.005	.006	$\pm .001$
8	10.0	20.0	.025	.023	- .002
9	0.25	12.5	.003	.0035	+ .0005
10	.25	12.5	.010	.009	- .001
11	.50	20.0	.030	.035	+ .005
Fe, mg.					
12	1.0	20.0	.000	.000	$\pm .000$
13	1.0	20.0	.005	.004	- .001
14	1.0	100.0	.025	.024	- .001
15	1.0	200.0	.060	.065	+ .005

With zinc alone, the gallium was determined directly in solutions having a pH and the salt concentrations previously given. (Results are shown in Table IV, numbers 1 to 5.) When zinc and aluminum were both present, the latter was separated by the procedure given under "The Determination of Gallium in the Presence of Aluminum," and the gallium determined as if zinc were absent. (Determina-

tions from 6 to 11 show the results obtained.) With iron and zinc present the procedure given under "The Determination of Gallium in the Presence of Iron" was followed except that sufficient sodium hydroxide was added to dissolve the zinc hydroxide. (Determinations 12 to 15 are representative of the results obtained.)

Numbers 4, 5, 10, 11, 14 and 15 were diluted to 100 ml. and aliquots taken for colorimetric comparison. In determinations 6, 7 and 8 the Na_3AlF_6 was filtered off before comparison, while in 9, 10 and 11 the comparison was made without prior filtration.

This shows that gallium can be determined in the presence of zinc if the ratio of zinc to gallium does not exceed 25,000 to 1, providing the solution contains 0.5 g. of sodium fluoride per liter. If the Na_3AlF_6 was not filtered off, as in determinations 9, 10 and 11, a color was produced if approximately the maximum amounts of both zinc and aluminum, which would give no color when alone, were present, but not when half that quantity of each element was present.

The Determination of Gallium in the Presence of Iron and Aluminum

It was not possible to precipitate the aluminum with sodium fluoride, after the separation of iron with an excess of sodium or potassium hydroxide, due to the interference of the large amount of alkali salts introduced. This made it necessary to acidify the solution after the removal of iron and precipitate the hydroxides of gallium and aluminum by ammonium hydroxide. If this precipitate was filtered on the best grade of filter paper it was found that traces of iron were extracted from the paper during the boiling with hydrochloric acid necessary to redissolve the hydroxides. To avoid this interference the solution was filtered through a Gooch crucible containing a mat of purified anthracene or phenanthrene.^{10,11}

Procedure.—The iron was separated as described under "The Determination of Gallium in the Presence of Iron and Indium" and the filtrate acidified with hydrochloric acid. The aluminum and gallium hydroxides were precipitated with ammonium hydroxide according to Blum's method¹² and filtered through a Gooch crucible containing an anthracene or phenanthrene mat, supported on a perforated disk.

(10) Gooch, *Proc. Am. Acad. Arts Sci., New Series*, **12**, 390 (1884-85).

(11) These latter substances were purified by dissolving in hot acetone and pouring slowly with constant agitation into an equal volume of concentrated hydrochloric acid. The precipitated anthracene or phenanthrene was filtered off and washed first with hot dilute hydrochloric acid and then with hot water. It was then crystallized from acetone or toluene. If this product, when boiled with hydrochloric acid, gave an extract which produced a color with quinalizarin under the conditions of the colorimetric determination, the process was repeated.

(12) Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).

TABLE V
SEPARATION OF GALLIUM FROM ALUMINUM AND IRON

No.	Al, mg.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10.0	1.0	0.000	0.000	±0.000
2	10.0	1.0	.005	.006	+ .001
3	10.0	1.0	.020	.020	± .000
4	10.0	1.0	.050	.045	- .005
5	15.0	1.0	.010	.008	- .002
6	1.0	1.0	.010	.008	- .002
7	0.5	1.0	.000	.000	± .000
8	.5	1.0	.005	.0055	+ .0005
9	.5	1.0	.010	.008	- .002
10	.5	1.0	.050	.045	- .005
11	.5	1.0	.030	.030	± .000

In Nos. 1-6, the Na_3AlF_6 was filtered off. In Nos. 7-11 no separation of the aluminum was made. Nos. 3, 4, 5, 6, 9, 10 and 11 were diluted to 100 ml. and aliquots taken for comparison.

The precipitate and mat were transferred to the original beaker and boiled with hydrochloric acid. The filtering medium was filtered off through a paper previously washed with 5 *N* hydrochloric acid. The aluminum was then separated by means of sodium fluoride and the gallium determination completed in the usual manner. If only a half milligram of aluminum or less was present, the gallium was determined directly without any separation from that element. The results are shown in Table V.

It is therefore possible to determine gallium in the presence of iron and aluminum when both of the latter are present in as large an amount as is permissible when either is present alone.

The Determination of Gallium in the Presence of Lead, Copper, Tin, Antimony, Germanium and Platinum

Procedure.—The strongly hydrochloric acid solution containing the above elements was distilled to remove germanium. The acidity of the remaining solution was adjusted so as just to prevent precipitation by hydrolysis, and stirred with a small excess of cadmium metal (40 to 60 mesh). The precipitated metals and excess of cadmium were filtered off, 2 to 3 ml. of concd. sulfuric acid added to the filtrate and evaporated to fumes to expel hydrochloric acid. Approximately 100 ml. of water was added and the cadmium removed by electrolysis. This was followed by treatment with hydrogen sulfide to remove the last traces of cadmium and any of the other metals which might be remaining. After filtration and washing, the filtrate was reduced in volume by evaporation, treated with an excess of sodium hydroxide, potassium permanganate, etc., and the determination completed as previously given.

By this method 0.01 mg. of gallium could be determined in the presence of 0.1 g. of each of the above metals either singly or as a mixture.

TABLE VI

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF LEAD, COPPER, TIN, ANTIMONY, GERMANIUM AND PLATINUM

No.	Milligrams	Ga taken, mg.	Ga found, mg.	Error, mg.
1	Pb 100	0.000	0.000	± 0.000
2	Pb 100	.010	.012	+ .002
3	Pb 100	.100	.090	- .010
4	Cu 100	.000	.000	$\pm .000$
5	Cu 100	.010	.010	$\pm .000$
6	Cu 100	.050	.050	$\pm .000$
7	Sn 100	.000	.000	$\pm .000$
8	Sn 100	.010	.012	+ .002
9	Sn 100	.050	.053	+ .003
10	Sb 100	.000	.000	$\pm .000$
11	Sb 100	.010	.011	+ .001
12	Sb 100	.050	.045	- .005
13	Sn 100 Sb 100	.000	.000	$\pm .000$
14	Sn 100 Sb 100	.010	.010	$\pm .000$
15	Sn 100 Sb 100	.050	.048	- .002
16	Pb 100 Cu 100	.000	.000	$\pm .000$
17	Pb 100 Cu 100	.010	.008	- .002
18	Pb 100 Cu 100	.100	.105	+ .005
19	Ge 30	.000	.000	$\pm .000$
20	Ge 30	.010	.008	- .002
21	Ge 30	.100	.107	+ .007
22	Ge 30	.000	.000	$\pm .000$
23	Ge 30	.010	.011	+ .001
24	Ge 30	.050	.050	$\pm .000$
25	Pt 20	.000	.000	$\pm .000$
26	Pt 20	.010	.012	+ .002
27	Pt 20	.050	.053	+ .003

In numbers 22, 23 and 24 the germanium was separated by precipitation as the sulfide.

A direct precipitation of more than a trace of the sulfide metals with hydrogen sulfide from a 0.3 *N* acid solution usually resulted in loss of gallium due to its being carried down with the sulfide precipitate, except with the small amount of germanium which was present. In this case, a quantitative separation was obtained by precipitating this element with hydrogen sulfide from 6 to 8 *N* hydrochloric acid. Results obtained are shown in Table VI.

General Procedure.—Obtain the substance in a hydrochloric acid solution and filter off any silver, lead and mercurous mercury which may have precipitated as chloride. Follow this by

the procedure given under "The determination of Gallium in the presence of Lead, Copper, Tin, Antimony, Germanium and Platinum." Next separate iron, indium and aluminum, and determine gallium according to the procedure given under "The determination of Gallium in the presence of Iron and Aluminum." This will remove all interfering elements except vanadium and molybdenum, for which no satisfactory separation was found. As much as 100 mg. of lead, copper, antimony, tin, zinc, indium and doubtless that much platinum and germanium may be present, but more than 10 mg. of aluminum and one milligram of iron cause difficulty.

Summary

1. A method for the colorimetric determination of gallium has been developed, based upon the formation of a pink to amethyst colored lake with quinalizarin. The optimum condition is a solution which is normal in ammonium acetate, 0.5 *N* in ammonium chloride, of *pH* 5.0 and containing 0.5 g. of sodium fluoride per liter. Under these conditions 0.02 mg. of gallium per liter can be distinguished. The best concentrations for comparison, using 50-ml. Nessler tubes, lie between 0.02 and 0.2 mg. of gallium per liter.

2. Methods have been developed for separating minute amounts of gallium from 100 mg. of those metals which interfere by giving colored lakes under the same conditions, namely, lead, copper, tin, antimony, indium, platinum and germanium, except that not more than 10 mg. of aluminum, nor 1 mg. of iron should be present, while vanadium and molybdenum must be absent.

